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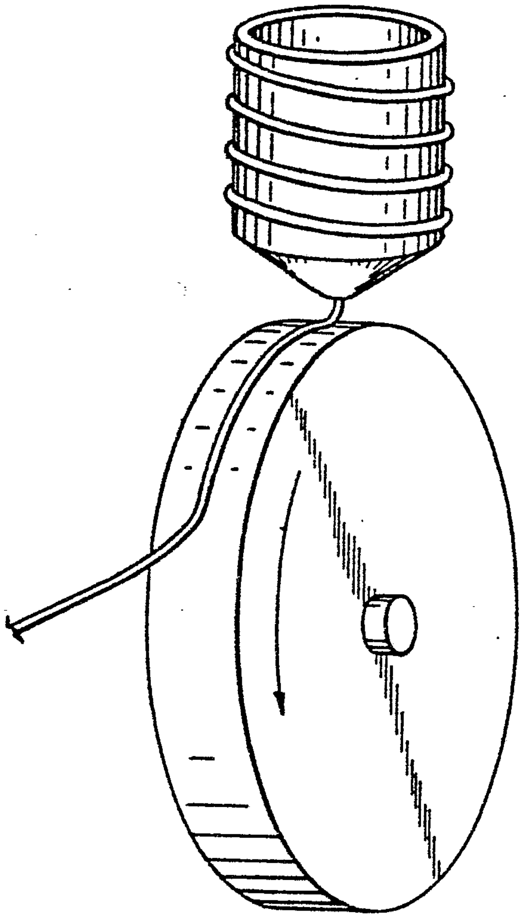
(54) Title: CHILL CASTING OF METAL STRIP EMPLOYING A MOLYBDENUM CHILL SURFACE

(57) Abstract

In the process of making metal strip directly from the melt by impinging molten metal onto the flat surface (3) of a rapidly moving chill body (1), the useful life of the chill body surface is prolonged, and strip surface properties are improved, by using a chill body having a surface of molybdenum.



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CHILL CASTING OF METAL STRIP EMPLOYING A MOLYBDENUM CHILL SURFACE

Cross-Reference to Related Application

This application is a continuation-in-part of my copending U.S. application Serial No. 904,945, filed May 11, 1978.

BACKGROUND OF THE INVENTION AND THE PRIOR ART

It is known to make flat, continuous metal strip, of crystalline as well as amorphous (glassy) structure, directly from the melt by impinging molten metal onto the flat surface of a rapidly moving chill body whereon it is quenched to the solid state. The chill body may be a rotating wheel or cylinder, and the molten metal may be impinged onto the flat peripheral surface of the wheel or onto the inner surface of the cylinder. The chill body may also be a traveling belt, usually an endless belt. The metal may be impinged onto the surface of the chill body by methods such as jetting the molten metal onto the surface.

It is also known to form metal filament directly from the melt by contacting a pendant, unconfined drop of molten metal with the V-shaped circumferential edge or lip of a rotating heat extraction member, as disclosed, for example, in U.S. Patents 3,896,203 to Maringer et al. and 4,124,664 to Maringer. The methods disclosed in these patents may employ a heat extracting edge or lip composed of metals such as copper, aluminum, nickel, molybdenum and iron. These methods, however, do not produce flat strip, but instead produce what appears to be rounded fibers, having opposed convex/concave surfaces.

The surface of the chill body must meet several requirements. First, it must be wetted by the molten metal, or else formation of continuous strip will not take place. Second, it must be non-reactive with the molten metal, that is to say the molten metal must not attack, and must not weld to the chill surface, or else the strip cannot be cleanly separated therefrom. Third, it must have good thermal conductivity to permit rapid removal of large amounts of heat as is necessary to effect rapid solidification of the molten metal. Lastly, it must have sufficient wear resistance in continuous production of metal strip by the above-described quench casting process. Wear resistance is an extremely important aspect of chill body performance. Wear resistance does not usually pose a problem in the above-described melt extraction processes, wherein metal fibers are drawn out of a pendant drop of molten metal. However, in the melt-spin process wherein molten metal is impinged on the chill surface, severe erosion of the chill surface usually results from a combination of factors, including the momentum of the impinging stream in combination with the high temperature of the molten metal.

High heat conductivity metals previously proposed to serve as chill body surface, such as copper, aluminum, beryllium copper or silver, do not have the desired wear characteristics. Others, such as stainless steel, which would be expected to have good wear characteristics, fall short in other respects, such as failure to provide sufficient wetting.

It is an object of the present invention to provide improved chill bodies for the quench casting process for making flat metal strip directly from the melt by impinging the molten metal onto the flat surface of a rapidly moving chill body.

SUMMARY OF THE INVENTION

In accordance with the present invention there is provided an improvement in the method for making flat metal strip directly from the melt by impinging the molten metal onto the flat surface of a rapidly moving chill body, which improvement comprises impinging the molten metal onto the flat surface of a chill body made of molybdenum.

The present invention further provides an improvement in the apparatus for making metal strip directly from the melt by impinging molten metal onto the flat surface of a rapidly moving chill body, which apparatus includes a chill body having a flat surface adapted to receive molten metal to be impinged thereon for rapid quenching together with means functionally connected with said chill body for impinging molten metal onto its surface, wherein the improvement comprises providing a chill body having a surface of molybdenum.

I have surprisingly found that the molybdenum chill surface is readily wetted by the molten metal - especially by iron, nickel or cobalt-based alloys which upon rapid quenching from the melt form amorphous structures. The molybdenum surface further provides for good adhesion of the solidified metal strip, which is essential to effect thorough quenching of the metal if a ductile, amorphous metal strip is desired, yet it also affords clean release of the solidified strip from the surface. Most importantly, the molybdenum surface has excellent wear-resistant properties as compared to chill surfaces previously used in the melt-spin process wherein molten metal is impinged onto the chill surface. In addition, the molybdenum has adequate heat conductivity to permit sufficiently rapid quenching, at rates in excess of 10^4 or 10^5 degrees centigrade per second, of thin layers of molten metal (in the order of a few thousands inch thickness), as is required for formation of amorphous metal strip.

The benefits of chill bodies having a molybdenum surface in the process of making flat metal strip directly from the melt by impinging the molten metal onto the rapidly moving flat surface of a chill body are obtained regardless of the configuration of the chill body. That is to say, the chill body may be a rapidly rotating drum having a flat exterior surface which serves as the chill surface; it may be a rapidly rotating cylinder whereof the flat inner surface furnishes the chill surface, a moving belt or any other suitable structure which provides a flat surface.

For purposes of the present invention, a flat strip is a slender body whose transverse dimensions are much less than its length, and whose thickness is much less than its width, typically having a width at least about ten times its thickness, and having smooth and even top and bottom surfaces which are generally parallel to each other.

A flat chill body surface is an endless surface provided by an endless belt, or the exterior or interior surface of a drum or cylinder, and which is smooth and even and which is straight in transverse direction, upon which a flat strip, as above-defined, may be cast.

BRIEF DESCRIPTION OF THE DRAWINGS

The annexed drawings further illustrate the present invention.

Fig. 1 is a cross-sectional view of an annular chill roll, the exterior surface of which is provided with a layer of molybdenum metal, to provide a casting surface of molybdenum.

Fig. 2 is a cross-sectional view of an annular chill roll having a ring of molybdenum inserted in its surface.

Fig. 3 is a cross-sectional view of a cylindrical chill body having an inner molybdenum-clad chill surface inclined with respect to the axis of rotation.

Fig. 4 is a side view in partial cross section showing means for jetting molten metal onto a rotating chill roll and a rotating chill roll provided with a chill surface of molybdenum metal.

Fig. 5 is a somewhat simplified perspective view of apparatus including means for depositing molten metal onto a chill surface in the form of a moving endless belt having a surface of molybdenum.

DETAILED DESCRIPTION OF THE INVENTION OF THE PREFERRED EMBODIMENTS AND OF THE BEST MODE PRESENTLY CONTEMPLATED FOR ITS PRACTICE

Chill casting processes for making flat metal strip - polycrystalline as well as amorphous (glassy) metal strip -

by impinging molten metal onto the flat surface of a rapidly moving chill surface of a heat extracting member (chill body) are well known. It has now been found that for use in such chill casting processes molybdenum has a desirable combination of properties required of a good chill surface, namely high melting point (2650°C); relatively low coefficient of thermal expansion (lower than that of copper); moderately high thermal conductivity (about 35% of that of copper); and moderately high hardness. It has further been found that molybdenum has the required wetting properties for the molten metal and release properties for the solidified strip which, in combination with the aforementioned properties, make it eminently suitable for use as chill surface in quench casting of amorphous metal strips, especially ductile amorphous metal strips. Most significant is the ability of molybdenum chill surfaces to resist erosion and wear by the impinging stream of molten metal, whether the casting takes place under vacuum or in a gaseous atmosphere, which may be air or a protective atmosphere such as nitrogen, helium and the like. This is in contrast to the presently employed copper chill surfaces.

When flat amorphous metal strips are made by jetting molten glass forming alloy against the surface of a rapidly rotating chill body as, e.g., described in U.S.P. 4,077,462 to Bedell et al., or in U.S.P. 3,856,074 to Kavesh, the surface of the chill body becomes gradually eroded. A rough, uneven track is developed around the periphery of the chill body surface whereon casting of the strip takes place. Further casting into the same track produces strip of unacceptable quality, having a rough surface and ragged edges. The problem of chill surface wear in these processes is even more acute when casting takes place under vacuum. The absence of an intervening gas layer in vacuum casting allows a larger area of the chill surface to be impacted and wetted by the molten jet. Another factor which leads to severe wear on conventional chill surfaces is inclusion in the alloy being cast of appreciable amounts of refractory metals, e.g., molybdenum, tungsten, chromium, hafnium, iridium, niobium, osmium, platinum, rhenium, rhodium, ruthenium, tantalum, thorium, vanadium, and zirconium. Hence, use of a chill surface of molybdenum is particularly advantageous when casting under vacuum (say under absolute pressure of less than about 1 in. Hg.), or when casting glass-forming alloys containing one or more refractory metals, and especially when casting such alloys under vacuum.

The form of the chill body and the mode of the casting operation are not critical for purposes of the present invention, so long as a flat casting surface is provided. For example, casting may take place against the peripheral surface of a rapidly rotating drum by jetting molten metal against that surface, as disclosed in the above-mentioned patents to Bedell et al. and Kavesh. The molten metal may be deposited under pressure from a slotted nozzle onto the flat chill surface, as described in U.S.P. 4,142,571 to Narasimhan. Furthermore, the chill surface may be furnished by the interior surface of a rotating cylinder, as described in U.S.P. 3,881,540 to Kavesh and U.S.P. 3,881,542 to Polk et al., or as shown by Pond and Maddin in Trans. Met. Soc. AIME, 245 (1969) 2,475-6.

The chill surface of molybdenum may, in accordance with the present invention, be provided by fabricating the chill body of molybdenum, or by merely providing a surface layer of molybdenum on a chill body constructed of other material, suitably material having high thermal conductivity, such as copper or silver. Chill bodies made of molybdenum may be fabricated employing methods usually employed for fabrication of molybdenum, including machining from solid stock, such as cast pieces, or fabrication by known powder metallurgical methods. A particularly desirable embodiment of the present invention is a composite chill body, especially a chill roll, made of copper provided with a hoop of molybdenum, as illustrated in Figs. 1 and 2. With reference to Fig. 1, chill roll 1 made of copper is mounted for rotation on shaft 2. The flat exterior surface of chill roll 1 is provided with a hoop of molybdenum 3. In Fig. 1, the hoop of molybdenum covers the total peripheral surface of the chill roll. With reference to Fig. 2, a narrower hoop of molybdenum 3 is provided covering only part of the peripheral surface of the chill roll. The molybdenum hoop may be affixed to the copper chill roll, e.g. by shrink fitting. Alternatively, a molybdenum surface may be provided by any other conventional surface coating method, as for example oxyacetylene spraying, a method which involves feeding a molybdenum wire into the cone of an oxygen/acetylene flame to melt the metal, and then propelling the molten metal in droplet form against the surface to be coated. Other suitable methods include plasma arc spraying and conventional cladding procedures.

Detailed design and construction of apparatus of the present invention is within the capability of any competent worker skilled in the art.

The following example further illustrates the present invention and sets forth the best mode presently contemplated for its practice.

Example 1

Apparatus employed was similar to that depicted in Fig. 4 employing a chill roll of construction as shown in Fig. 2. The chill roll had an outer diameter of 8 inches, and its quench surface was 0.5 inches wide. It was rotated at a speed of about 2000 rpm. The apparatus was enclosed in a vacuum chamber. All tests were conducted under vacuum of about 100 mm. Concurrent experiments employing a chill roll made of copper having an outer diameter of 8 inches and a width of 1 inch rotated at 2000 rpm, were conducted, also under vacuum of about 100 mm. A number of different glass forming alloys (alloys which upon rapid quenching from the melt, at a rate in excess of about 10^4 to 10^5°C/sec. form an amorphous solid structure (see, e.g. U.S.P. 3,856,513 to Chen and Polk) having melting points in excess of 1,500°C were cast by jetting the molten metal against the rotating chill surface through an orifice of 0.025 inch diameter under pressure of 5 psig. It was difficult to cast continuous ductile strips on the copper chill surface. In all cases the molten alloys attacked the copper chill surface, causing erosion, cracking and pitting. The chill surface so roughened caused subsequent mechanical locking of pieces of strip onto the chill surface along the track where the strip was cast. The pieces of strip welded to or mechanically interlocked with the chill surface, causing disintegration of the molten puddle on the chill surface, and prevented subsequent formation of continuous strip on the same track. The yield of usable strip was very low. In contrast thereto the same alloys, when cast on a molybdenum chill surface, yielded good quality ribbon. The comparative results are summarized in Table 1, below.

TABLE I

Results of Chill Casting of 30 gms of Molybdenum and Tungsten Base Glassy Alloys on Copper and Molybdenum Chill Surfaces

Copper Chill Surface

Alloy Composition (atom percent)	Ribbon Fabric-ability	Ribbon Character-istics	Chill Surface Condition after Casting	Yield of Ribbon
$Mo_{40}Co_{40}B_{20}$	extremely poor	discontinous -rough edge	gorged;metal pieces welded to surface	2%
$Mo_{40}Fe_{40}B_{20}$	"	"	"	2%
$Mo_{50}Co_{30}B_{20}$	"	"	"	"
$Mo_{50}Fe_{30}B_{20}$	"	"	"	"
$Mo_{60}Fe_{20}B_{20}$	"	"	"	"
$Mo_{65}Fe_{15}B_{20}$	"	"	"	"
$W_{40}Fe_{20}Co_{20}B_{20}$	"	"	"	"
$W_{40}Ni_{50}B_{10}$	"	"	"	"
$Mo_{45}Ni_{45}B_{10}$	"	"	"	"
$W_{40}Co_{50}B_{10}$	"	"	"	"
$Mo_{60}Co_{20}B_{20}$	"	"	"	"
$Mo_{30}W_{20}Fe_{30}B_{20}$	"	"	"	"
$Mo_{45}Fe_{10}Ni_{10}Co_{15}B_{20}$	"	"	"	"
$Mo_{50}Fe_{20}Co_{10}B_{20}$	"	"	"	"
$Mo_{40}Fe_{20}Co_{20}B_{20}$	"	"	"	"
$Fe_{47}W_{35}B_{18}$	"	"	"	"
$Mo_{40}Fe_{33}Cr_{7}B_{20}$	"	"	"	"
$W_{40}Fe_{50}B_{10}$	"	"	"	"
$Fe_{40}W_{40}B_{20}$	"	"	"	"
$Ni_{50}Mo_{30}B_{20}$	"	"	"	"

TABLE I (Continued)

Results of Chill Casting of 30 gms of Molybdenum and Tungsten Base Glassy Alloys on Copper and Molybdenum Chill Surfaces

Molybdenum Chill Surface

Alloy Composition (atom percent)	Ribbon Fabric-ability	Ribbon Character-istics	Chill Surface Condition after Casting	Yield of Ribbon
$Mo_{40}Co_{40}B_{20}$	Excellent	Continuous-good edge & surface	Insignificant wear	90%
$Mo_{40}Fe_{40}B_{20}$	"	"	"	"
$Mo_{50}Co_{30}B_{20}$	"	"	"	"
$Mo_{50}Fe_{30}B_{20}$	"	"	"	"
$Mo_{60}Fe_{20}B_{20}$	"	"	"	"
$Mo_{65}Fe_{15}B_{20}$	"	"	"	"
$W_{40}Fe_{20}Co_{20}B_{20}$	"	"	"	"
$W_{40}Ni_{50}B_{10}$	"	"	"	95%
$Mo_{45}Ni_{45}B_{10}$	"	"	"	"
$W_{40}Co_{50}B_{10}$	"	"	"	"
$Mo_{60}Co_{20}B_{20}$	"	"	"	90%
$Mo_{30}W_{20}Fe_{30}B_{20}$	"	"	"	"
$Mo_{45}Fe_{10}Ni_{10}Co_{15}B_{20}$	"	"	"	"
$Mo_{50}Fe_{20}Co_{10}B_{20}$	"	"	"	"
$Mo_{40}Fe_{20}Co_{20}B_{20}$	"	"	"	"
$Fe_{47}W_{35}B_{18}$	"	"	"	"
$Mo_{40}Fe_{33}Cr_{7}B_{20}$	"	"	"	"
$W_{40}Fe_{50}B_{10}$	"	"	"	"
$Fe_{40}W_{40}B_{20}$	"	"	"	"
$Ni_{50}Mo_{30}B_{20}$	"	"	"	"

Example 2

Following the general procedure of Example 1, 50 gram portions of molten, glass-forming alloy of the composition $Fe_5Ni_{45}B_{16}Mo_4Cr_{10}Co_{20}$ (atom percent) were impinged (squirted) onto the flat peripheral surface of chill rolls of 8-12 in. diameter fabricated of different materials of construction and the quality of the strip (whether or not ductile, glassy metal strip was obtained), and chill surface wear and casting qualities were visually observed. Results are summarized in Table 2, below.

Table 2

Chill Surface Material	Makes Ductile Strip	Remarks:
Nickel	No	Melt welds to substrate at spots, jet breaks up on impingement.
Monel™ ($Ni_{60}Cu_{40}$)	Yes	Only limited lengths; melt welds to substrate as beads.
Cupronickel	No	Melt does not wet, puddle breaks up.
Stainless 304 Cold Rolled Mild Steel	No	Same as above.
Tool Steel (hardened)	No	Melt welds to the substrate at spots.
Chromplate (.001") on Hardened Tool Steel	Yes	Makes continuous ribbons, no spalling of chromium
Invar™ (Fe-Ni)	No	Melt welds to the substrate.
Chromeplate (.001") on Invar™	Yes	Makes good ribbon, no spalling of chromium.
Chromeplate (.001") on Copper	Yes	Only limited lengths, chromium spalls off afterwards.
Molybdenum (hot pressed, 95% dense)	Yes	Makes continuous ribbons.
BeO (hot pressed 90% dense)	No	Puddle breaks up.
Pyrex™	No	Puddle breaks up.
Tungsten (chemical vapor deposited 100% dense)	Yes	Makes ribbon.
Platinum	No	Puddle breaks up, melt does not wet the substrate.

Since various changes and modifications may be made in the invention without departing from the scope and essential characteristics thereof, it is intended that all matter contained in the above description shall be interpreted as illustrative only, the invention being limited only by the scope of the appended claims.

I claim:

1. In the method for making metal strip directly from the melt by impinging molten metal onto the surface of a rapidly moving chill body, the improvement which comprises impinging the molten metal onto the flat surface of a chill body made of molybdenum to quench the metal into a flat strip.

2. The improvement of claim 1 wherein the metal strip is of predominantly amorphous structure.

3. The improvement of claim 2 conducted under vacuum of absolute pressure of less than about 1 inch Hg.

4. The improvement of claim 2 wherein the molten metal is an alloy containing one or more refractory metals.

5. The improvement of claim 4 conducted under vacuum of absolute pressure of less than about 1 inch Hg.

6. Apparatus for making metal strip directly from molten metal by impinging the molten metal onto the flat surface of rapidly moving chill body, comprising a chill body having a flat surface of molybdenum adapted to receive molten metal to be impinged thereon for rapid quenching to the solid state, together with means functionally cooperating with said chill body for impinging molten metal onto its surface.

7. The improved apparatus of claim 6 enclosed in a vacuum chamber.

8. The improved apparatus of claim 6 having a chill body of copper provided with a chill surface of molybdenum.

9. The improved apparatus of claim 6 wherein the chill body is an annular chill roll having a peripheral chill surface of molybdenum.

10. The improved apparatus of claim 6 wherein the chill body is a cylindrical chill body having an internal chill surface of molybdenum.

11. The improved apparatus of claims 9 or 10 wherein the chill body is constructed of copper and is provided with a chill surface of molybdenum.

FIG. 1

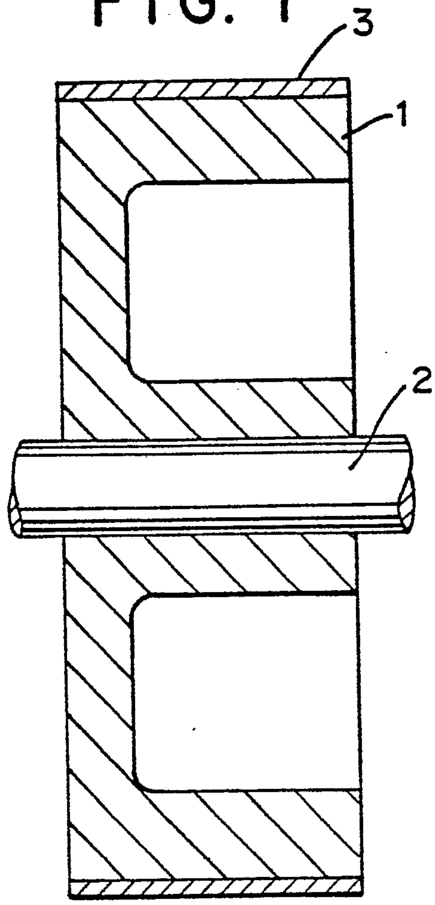


FIG. 2

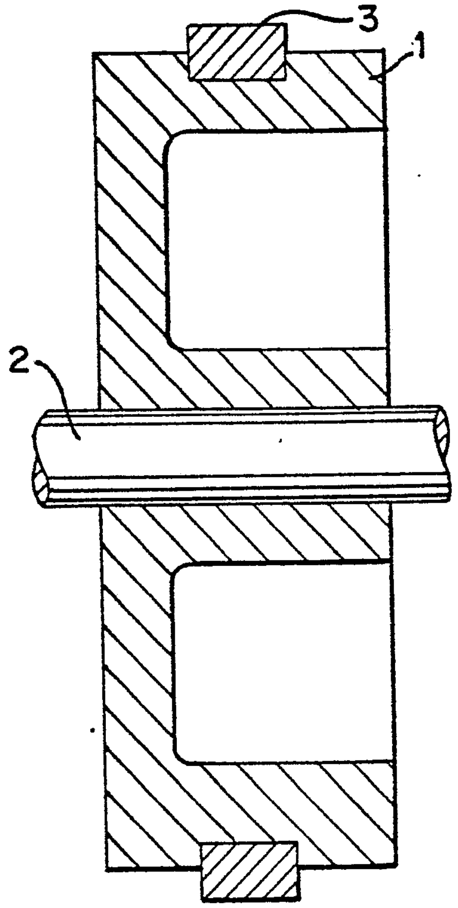


FIG. 3

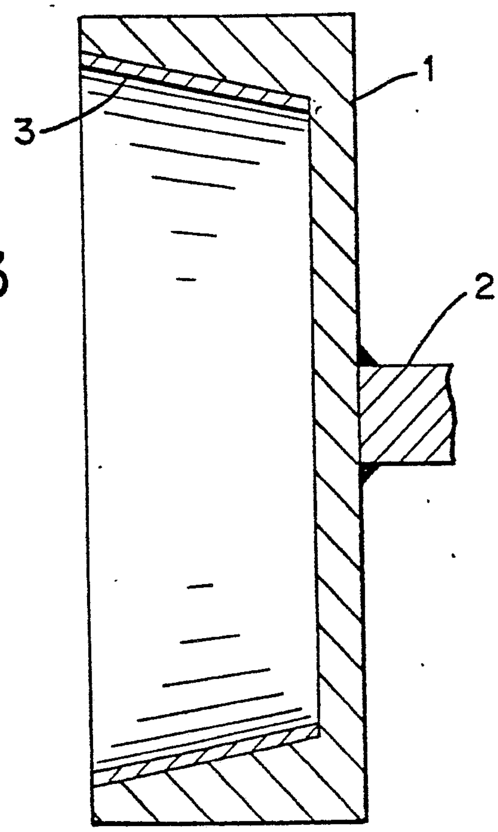
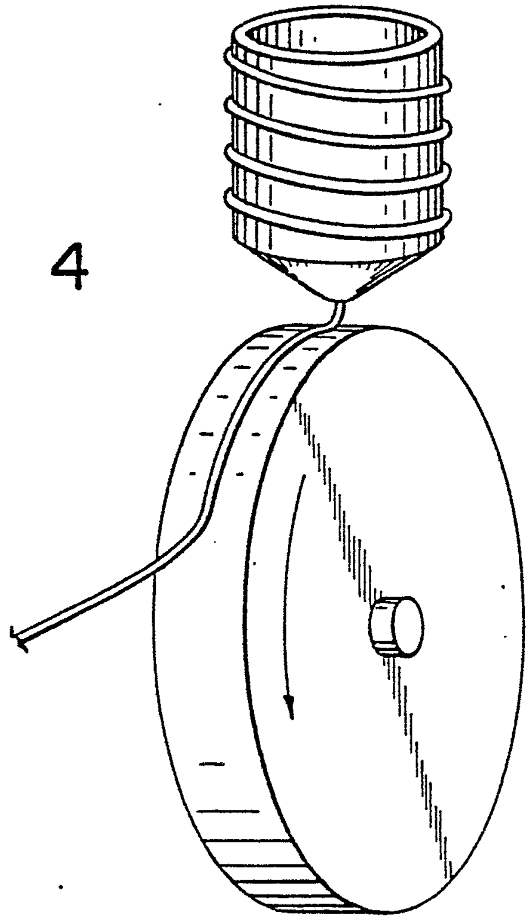


FIG. 4



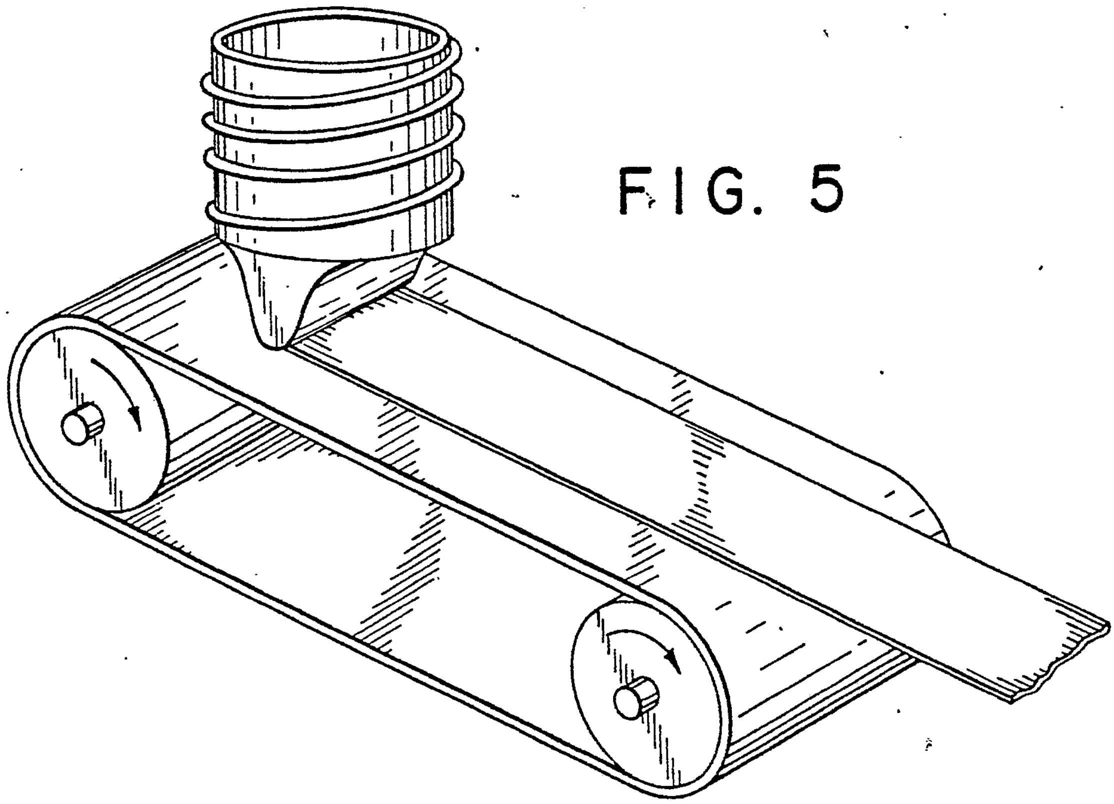


FIG. 5

INTERNATIONAL SEARCH REPORT

WO 79/01054

International Application No PCT/US79/00303

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL. B22D 11/06, 11/10
U.S. CL. 164/64,87,427,429

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	164/64,87,138,423,427,428,429

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X,P	US, A, 4,142,571, Published 06 March 1979, Column 7,line 65-Column 8,line 11, Narasimhan	1-9,11
X	US, A, 3,896,203, Published 22 July 1975, Column 6,lines 12-14, Maringer et al	1-11
X,P	US, A, 4,124,664, Published 07 November 1978, Column 8,lines 55-57, Maringer	1-11
X	DE, A, 2,719,710, Published 24 November 1977, Page 12,line 13-Page 13, line 15, Allied Chemical Corp.	1-8,10-11
A	US, A, 4,077,462, Published 07 March 1978, Column 4,lines 22-35, Bedell et al.	1-9,11
A	US, A, 3,881,540, Published 06 May 1975, KAVESH	1-8,10-11

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"X" document of particular relevance

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
09 JULY 1979	04 SEP 1979
International Searching Authority [1]	**Signature of Authorized Officer [20]**
ISA/US	J. Reed Batten Jr. J. REED BATTEN, JR.